

# PATENT SPECIFICATION

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(19)



## (54) PURIFICATION OF ACRYLONITRILE

(71) We, BP CHEMICALS INTERNATIONAL LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to a process for the purification of acrylonitrile.

Processes for the production of acrylonitrile by the vapour phase, catalytic reaction of acrolein, or substances giving rise to acrolein under the reaction conditions, e.g. propylene or allyl alcohol, molecular oxygen and ammonia are well known. In such processes it is also well known to produce acrolein and hydrogen cyanide as by-products. The presence of these by-products in the acrylonitrile product even in small traces is undesirable; for example, the presence of acrolein will interfere with the polymerisation of the nitrile if this is subsequently desired. Various attempts have been made to remove the by-products by careful fractional distillation but these attempts were not successful. It is known from British Patent Specification No. 719 635 (The Distillers Co. Ltd.) to treat the crude acrylonitrile containing the acrolein and hydrogen cyanide by-products with an alkaline compound such as sodium hydroxide to promote the reaction between the acrolein and hydrogen cyanide to produce the condensation product, acrolein cyanhydrin. This product which has a low volatility may then more easily be separated from acrylonitrile by distillation. This process suffers, however, from a disadvantage that unless the quantity of the alkaline compound employed is very carefully controlled a number of unwanted side-reactions occur.

It is the object of the present invention to provide a process for the purification of acrylonitrile in which the aforesaid disadvantages are substantially obviated.

Accordingly the present invention is a

process for the purification of acrylonitrile produced by the vapour phase reaction of acrolein, or a substance giving rise to acrolein under reaction conditions, molecular oxygen and ammonia at an elevated temperature in the presence of a catalyst and containing amounts of acrolein and hydrogen cyanide as by-products which comprises treating the impure acrylonitrile with an ammonium, alkali metal or alkaline earth metal salt of a weak aliphatic carboxylic acid to cause acrolein and hydrogen cyanide to react to form acrolein cyanhydrin and separating the acrolein cyanhydrin so formed from the acrylonitrile by distillation.

As already indicated substances giving rise to acrolein under the reaction conditions may be propylene or allyl alcohol. The catalyst employed may be any catalyst known for use in this reaction, many of which are referred to in "Propylene and its Industrial Derivatives" edited by E. G. Hancock, 1973, pages 423 to 425. Suitable ammonium, alkali metal or alkaline earth metal salts include the acetates, propionates, butyrates and stearates. By "alkaline earth metal" herein is included the metal magnesium. The preferred salt is ammonium acetate.

Treatment of the crude acrylonitrile with the ammonium, alkali metal or alkaline earth metal salt may be in a convenient manner. Thus the salt may be added as a solid or in aqueous or organic solutions to the crude acrylonitrile. Thus, for example, the preferred salt, ammonium acetate, may be added in the form of an aqueous solution of concentration for example 0.1 to 1500 g/litre of water, preferably 1.5 g/litre of water. The relative amount of ammonium acetate used for the treatment is not critical and may vary for example in volume ratio of crude acrylonitrile to aqueous ammonium acetate solution from 1000:1 to 1:1 depending on the desired rate of reaction. Generally a ratio of about 10:1 to 20:1 will be used. The treatment may be carried out at ambient temperature.

The contact time of the salt with the

impure acrylonitrile will vary according to the salt concentration, the volume ratio of acrylonitrile to salt solution (if used in this form) and the temperature. Generally a contact time within the range of 0.5 to 10 hours will be used.

When the reaction between the acrolein and hydrogen cyanide is completed the organic phase is separated, preferably stabilised by the addition of acid, e.g. toluene sulphonic acid, and is then distilled to separate the purified acrylonitrile and residual hydrogen cyanide (since this is usually present in excess amount relative to the acrolein) from the acrolein cyanhydrin. The ammonium or metal salt may be recovered and recycled for further use.

The process of the present invention is described in detail with reference to the following examples.

#### Example 1

An aqueous solution (100 ml) of ammonia acetate (1500 g/l) was stirred continuously at 38°C with 100 ml of crude acrylonitrile produced by the vapour phase reaction of acrolein molecular oxygen and ammonia at an elevated temperature in the presence of a catalyst and containing hydrogen cyanide 100 ppm succinonitrile and 5000 ppm acrolein. After 200 minutes the free acrolein concentration had fallen to less than 5 ppm and the temperature was still 38°C having remained constant throughout the test. The absence of side reactions was confirmed by the succinonitrile concentration remaining steady at 100 ppm. The acrolein cyanhydrin formed in the reaction was removed by distillation.

#### Example 2

Equal volumes of crude acrylonitrile as used in Example 1 and a solution of ammonium acetate (1500 g/litre) in water was stirred continuously. The free acrolein concentration fell from 2000 ppm to less than 5 ppm in 15 minutes. In a duplicate test but with deionised water in place of the ammonium acetate solution the free acrolein concentration after 15 minutes was 1500 ppm. The carbon cyanhydrin found in the reaction was removed by distillation.

#### Example 3

Crude acrylonitrile (10 volumes) as used in Example 1 was shaken with 1 volume of an aqueous solution of ammonium acetate (1 g/litre). The free acrolein concentration

fell from 2000 ppm to less than 5 ppm in 200 minutes. In a duplicate test but with deionised water in place of the ammonium acetate solution the free acrolein concentration was still 2000 ppm after 500 minutes. The acrolein cyanhydrin formed in the reaction was removed by distillation.

#### WHAT WE CLAIM IS:—

1. A process for the purification of acrylonitrile produced by the vapour phase reaction of acrolein, or a substance giving rise to acrolein under reaction conditions, molecular oxygen and ammonia at an elevated temperature in the presence of a catalyst and containing amounts of acrolein and hydrogen cyanide as by-products which comprises treating the impure acrylonitrile with an ammonium, alkali metal or alkaline earth metal salt of a weak aliphatic carboxylic acid to cause acrolein and hydrogen cyanide to react to form acrolein cyanhydrin and separating the acrolein cyanhydrin so formed from the acrylonitrile by distillation.

2. A process as claimed in claim 1 wherein the ammonium, alkali metal or alkaline earth metal salt is an acetate, propionate, butyrate or stearate.

3. A process as claimed in claim 1 or 2 wherein the salt is contacted with the impure acrylonitrile in the form of a solid or as an aqueous or organic solution.

4. A process as claimed in claim 3 wherein the salt is ammonium acetate in aqueous solution of concentration 0.1 to 1500 g/litre of water.

5. A process as claimed in claim 4 wherein the impure acrylonitrile is contacted with the aqueous ammonium acetate solution in volume ratio 10:1 to 20:1.

6. A process as claimed in any one of the preceding claims wherein the impure acrylonitrile is contacted with the ammonium or metal salt for a period of 0.5 to 10 hours.

7. A process for the purification of acrylonitrile as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

8. Acrylonitrile whenever purified by a process according to any one of the preceding claims.

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